Electricity is Different

Bob Eisenberg

Penn State August 2016

‘Charge’ is an Abstraction
with
VERY different Physics
in different systems

For me (and maybe few others)

Cezanne's

Mont Sainte-Victoire*

vu des Lauves

is a

Miracle

*one of two at Philadelphia Museum of Art 

See the fraternal twins

(i.e., not identical)

in the

Philadelphia Museum of Art

it is worth a visit,
and see the Barnes as well

Incomparable

Barnes Foundation

Philadelphia

Electricity is Different

Continuity of Current is a Miracle because

It is EXACT and UNIVERSAL

even though

Physics of Current Flow Varies Profoundly

Electricity is Different

Density and Concentration Fields are Weak

One percent **change in density does almost nothing**

The Electric Field is Strong

One percent **change in charge lifts the Earth,**

The Electric Field is Strong

If you were standing at arm's length from someone and each of you had

***One percent* more electrons than protons,**

the force
would lift the

Entire Earth!

slight paraphrase of third paragraph, p. 1-1 of
Feynman, R. P., R. B. Leighton, and M. Sands. 1963. *The Feynman: Lectures on Physics, Mainly Electromagnetism and Matter.* New York: Addison-Wesley Publishing Co.,
also at *http://www.feynmanlectures.caltech.edu/II_toc.html.*

Electricity is Different

Maxwell Equations

are **Universal** and **Exact**

$$\nabla \cdot \mathbf{E} = \frac{\rho}{\varepsilon_0}$$

What is this?
NOT exact
NOT universal

$$\nabla \cdot \mathbf{B} = 0$$

What is this?
NOT exact
NOT universal

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$$

$$\nabla \times \mathbf{B} = \mu_0 \mathbf{J} + \mu_0 \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t}$$

Displacement Current
Everywhere!
Inside atoms

As written by Heaviside, using Gibbs notation

$\mathbf{E}$ is electric field, $\mathbf{B}$ is magnetic field

$\mathbf{J}$ is the current of particles with mass

ρ is charge density (of all types)

ε_0 is the permittivity of a vacuum

μ_0 is the permeability of a vacuum

$(\mu_0 \varepsilon_0)^{-1/2} =$ velocity of light (!)

$\nabla \times$ is the **curl** operator

$\nabla \cdot$ is the **divergence** operator

Generalized Current is Conserved

Maxwell Equation

$$\nabla \times \mathbf{B} = \mu_0 \mathbf{J} + \mu_0 \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t}$$

What is this?
NOT exact
NOT universal

Displacement Current
Everywhere!
Inside Atoms

Vector Identity

Conservation law

$$\nabla \cdot \nabla \times \mathbf{B} \equiv 0; \quad \text{so,} \quad \nabla \cdot \underbrace{\left(\mathbf{J} + \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t} \right)} = 0$$

Generalized Current
EXACT & UNIVERSAL

Maxwell Equation $\nabla \times \mathbf{B} = \mu_0 \mathbf{J} + \mu_0 \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t}$ implies

$\mathbf{J} + \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t}$ **is conserved EXACTLY and UNIVERSALLY**

$$\mathbf{J} + \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t}$$

is conserved EXACTLY and UNIVERSALLY

Technical Comment

Description of charge ρ is problematic because it exists in so many forms with such complex properties. Universal representation of ρ does not exist!

Conservation of current does NOT depend on the properties of charge.

Conservation of current depends on the existence of $\mathbf{J}$ but not on its properties.
$\mathbf{J}$ exists if magnetism $\mathbf{B}$ exists.

Displacement Current $\varepsilon_0 \partial \mathbf{E}/\partial t$ occurs in vacuum. Atoms and matter are mostly vacuum. Only nuclei of atoms contain mass and they are tiny radius 10^{-15} m, atom is 10^{-10} m. Volume of nucleus/volume of atom is about 10^{-15}.

Maxwell Equations are Special

Continuity of Current is Exact and Universal

no matter what carries the current

even though

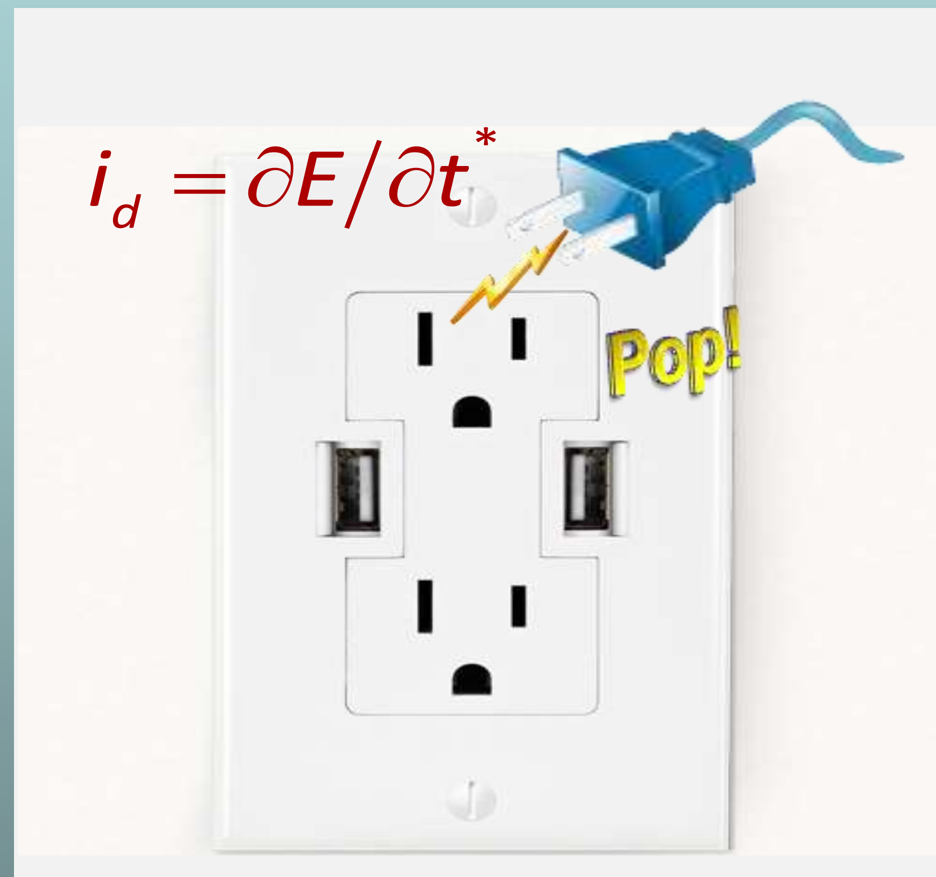
Physics of Charge Flow
Varies Profoundly
even Creating Plasmas!

'Charge' is an Abstraction
with
VERY different Physics
in different systems

Mathematics of Continuity
in Maxwell equations can
Create New Kind of Physics,
New Kind of Charge

When we unplug a computer power supply,
we often
CREATE
SPARKS,
i.e., a ***PLASMA,***

a ***NEW KIND***
of current flow



Physics of Charge Flow

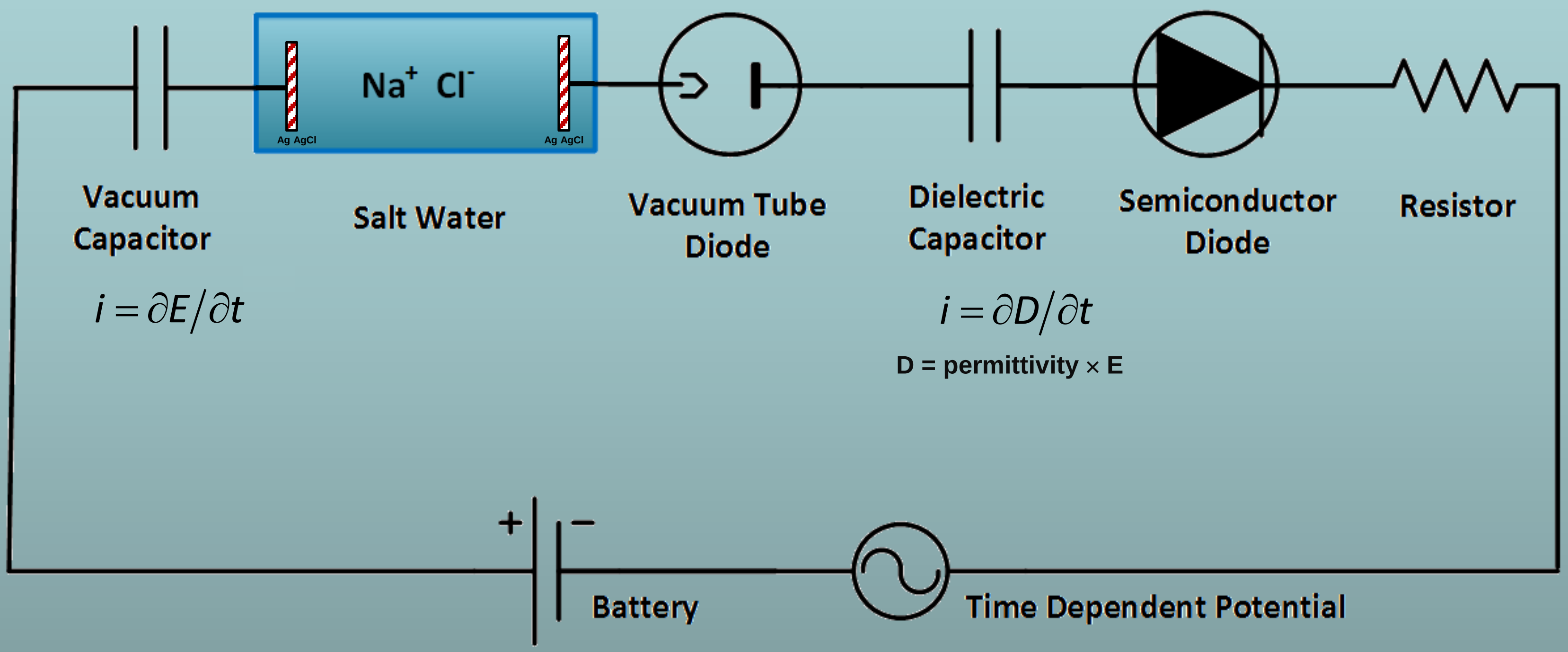
Varies Profoundly

but

Conservation of Current is EXACT and UNIVERSAL

'Charge' is an Abstraction

with different Physics in different systems



but **Conservation of Current** is **EXACT** and **UNIVERSAL**

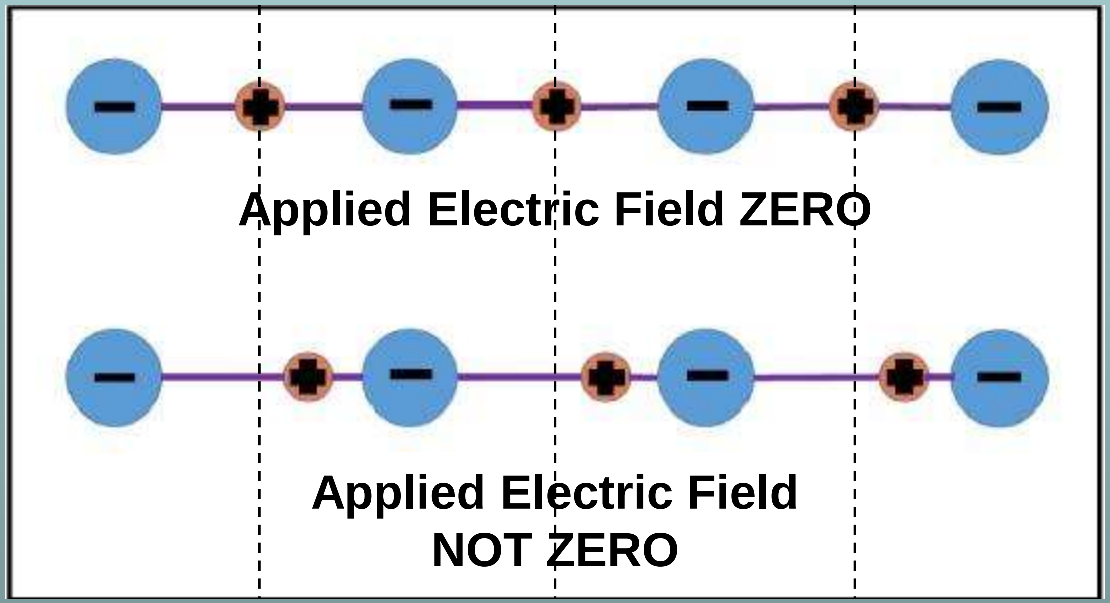
No matter what 'charge' carries the current!

Discussed in Detail in http://arxiv.org/abs/1502.07251

‘Charge’ is an Abstraction
with different Physics
in different systems

but **Conservation of Current is**
EXACT and UNIVERSAL
No matter what ‘charge’ carries the current!

Electrodynamics
and
Ions in Chemistry



Law of Mass Action

is how chemists have described chemicals,

not flows

$$A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B$$

$$-\frac{d}{dt}[A] = k_f\,[A]; \qquad -\frac{d}{dt}[B] = k_b\,[B]$$

k is constant

[A] means the activity or approximately the concentration of species A,
i.e., the number density of A

“ … incomplete truths
learned on the way
may become ingrained

and taken as the whole truth…….

what is true
and what is only sometimes true
will become confused.”

Richard Feynman
from p.15-61 “The Feynman: Lectures on Physics, Mainly Electromagnetism and Matter. Vol. 2” 1963, New York: Addison-Wesley Publishing Co., also at available on line

Law of Mass Action

is about

Conservation of Mass and Matter

It is not about conservation of charge

$$X \underset{k_{yx}}{\overset{k_{xy}}{\rightleftarrows}} Y \underset{k_{zy}}{\overset{k_{yz}}{\rightleftarrows}} Z$$

$$J_{xy}^{net} = J_{xy} - J_{yx}$$

$$= k_{xy}\left[X\right] - k_{yx}\left[Y\right]$$

$$I_{xy} = z_x F k_{xy}\left[X\right] - z_y F k_{yx}\left[Y\right]$$

[X] means the concentration, really activity of species Z, i.e., concentration is the number density

$$X \underset{k_{yx}}{\overset{k_{xy}}{\rightleftarrows}} Y \underset{k_{zy}}{\overset{k_{yz}}{\rightleftarrows}} Z$$

$$I_{xy} = z_x F k_{xy}[X] - z_y F k_{yx}[Y] \neq 0$$

$$I_{xy} \neq 0$$

[X] means the concentration, really activity of species Z, i.e., concentration is the number density

Kirchoff Current Law

requires

$$I_{AB} = I_{DE}$$

under all conditions

ALWAYS $\pm 10^{-17}$ *, or so*

Kirchoff Current Law

and

Maxwell Equations

are nearly the same thing

Bhat & Osting (2011). IEEE Trans Antennas and Propagation 59: 3772-3778

Heras (2007) American Journal of Physics 75: 652-657

Heras (2011) American Journal of Physics 79: 409

Itzykson & Zuber <u>Quantum Field Theory</u> (1990) p. 10

‘Current-in’

does not automatically equal

‘Current-out’

in Rate Models

if rate constants are independent

and

Currents are Uncorrelated

$$I_{AB} \neq I_{DE}$$

$$A \underset{k_{AB}}{\overset{I_{AB}}{\rightleftharpoons}} B \underset{k_{BC}}{\rightleftharpoons} C \underset{k_{CD}}{\rightleftharpoons} D \underset{k_{DE}}{\overset{I_{DE}}{\rightleftharpoons}} E$$

but **Kirchoff Current Law**

requires

$$\boldsymbol{I_{AB} = I_{DE}}$$

Electricity is Different

Correlation

between currents

is in fact

ALWAYS

0.999 999 999 999 999 999

because

Continuity of Current is Exact

Kirchoff Continuity of Current Law

including displacement current

is another form of Maxwell's Equations

Heras, J.A.: Am J Phys 75: 652 (2007); Eur J Phys 30: 845 (2009); Am J Ph79: 409 (2011)

Engineering

is about

Signal Flow

not chemicals

How can this be?

Chemistry

is about

Chemicals

not signals

Maxwell's Equations

Kirchoff's Current Law

compute

Signals

from Conservation of Charge

and

Continuity of Current,

including displacement current

Parameterization is not Possible

under more than one condition

Rate constants chosen at one boundary charge or one potential cannot work for different charges or potentials

Currents in Rate Models

are

Independent of Charge and Potential

but

in the real world

Currents depend on Charge and Potential

Cause of Frustration

Biochemical Models are

Rarely TRANSFERRABLE
Do Not Fit Data

even approximately

in more than one solution*

ESSAY

ASBMB Today (2014) 13:36-38
extended in http://arxiv.org/abs/1409.0243

Shouldn't we make biochemistry an exact science?

By Bob Eisenberg

Title chosen by Editor Charlie Brenner

Editors: Charlie Brenner, Angela Hopp
American Society for Biochemistry and Molecular Biology

***i.e., in more than one concentration or type of salt, like Na^+Cl^- or K^+Cl**

Note: Biology occurs in different solutions from those used in most measurements

Physical Chemists are Frustrated by Real Solutions

All of Biology occurs in Salt Solutions

of definite composition and concentration
and that matters!

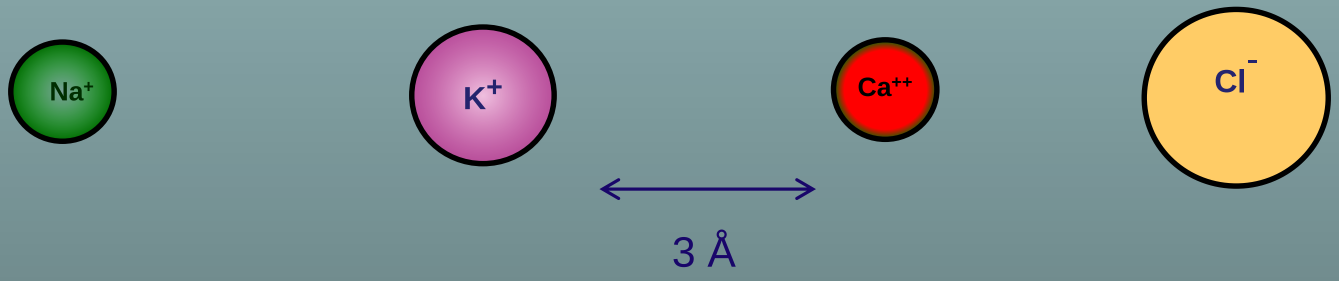
Salt Water is the Liquid of Life

Pure H_2O is toxic to cells and molecules!

Salt Water is a Complex Fluid

Main Ions are Hard Spheres, close enough

Sodium Na^+ Potassium K^+ Calcium Ca^{2+} Chloride Cl^-



“Sometimes it is necessary to put a veil on the past, For the Sake of the Future”

Henry Clay, the Essential American
p. 375 D.S. & J.T. Heidler

Ions

in a solution are a

Highly Compressible Plasma

although the

Solution is Incompressible

Free energy of an ionic solution is mostly determined by the
Number density of the ions.
Density varies from 10^{-11} to 10^{1}M
in typical biological system of proteins, nucleic acids, and channels.

Learned from Doug Henderson, J.-P. Hansen, Stuart Rice, among others…Thanks!

Electrolytes are Complex Fluids

Treating a

Complex Fluid

as if it were a

Simple Fluid

will produce

Elusive Results

It is not surprising that

Inconsistent Treatments

of ionic solutions

have been so

Unsuccessful

despite more than a century of work by fine scientists and mathematicians

Werner Kunz:

"It is still a fact that over the last decades,

it was easier to fly to the moon

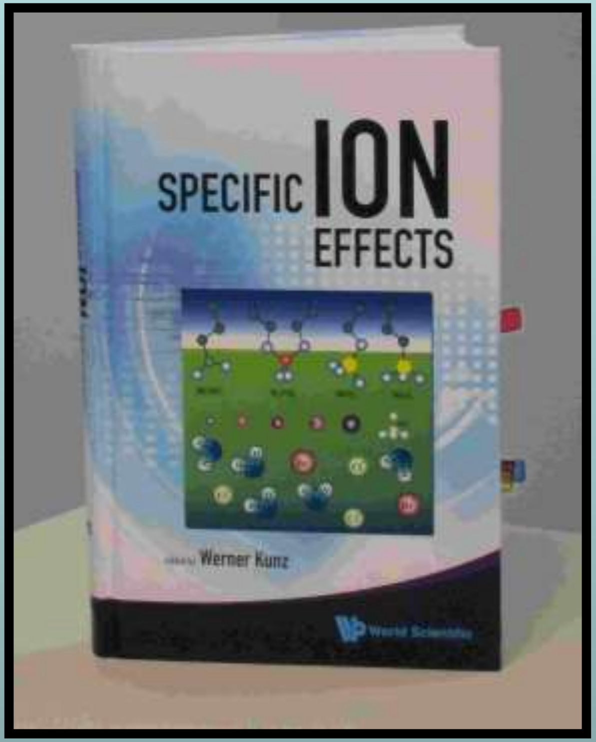
than to describe the

free energy of even the simplest salt solutions

beyond a concentration of 0.1M or so."

Kunz, W. "**Specific Ion Effects**"

World Scientific Singapore, 2009; p 11.



Kunz, W. "**Specific Ion Effects**"
World Scientific Singapore, 2009; p 11.

Werner Kunz

"It is still a fact that over the last decades,

it was easier to fly to the moon

than to describe the

free energy

of even the simplest salt solutions

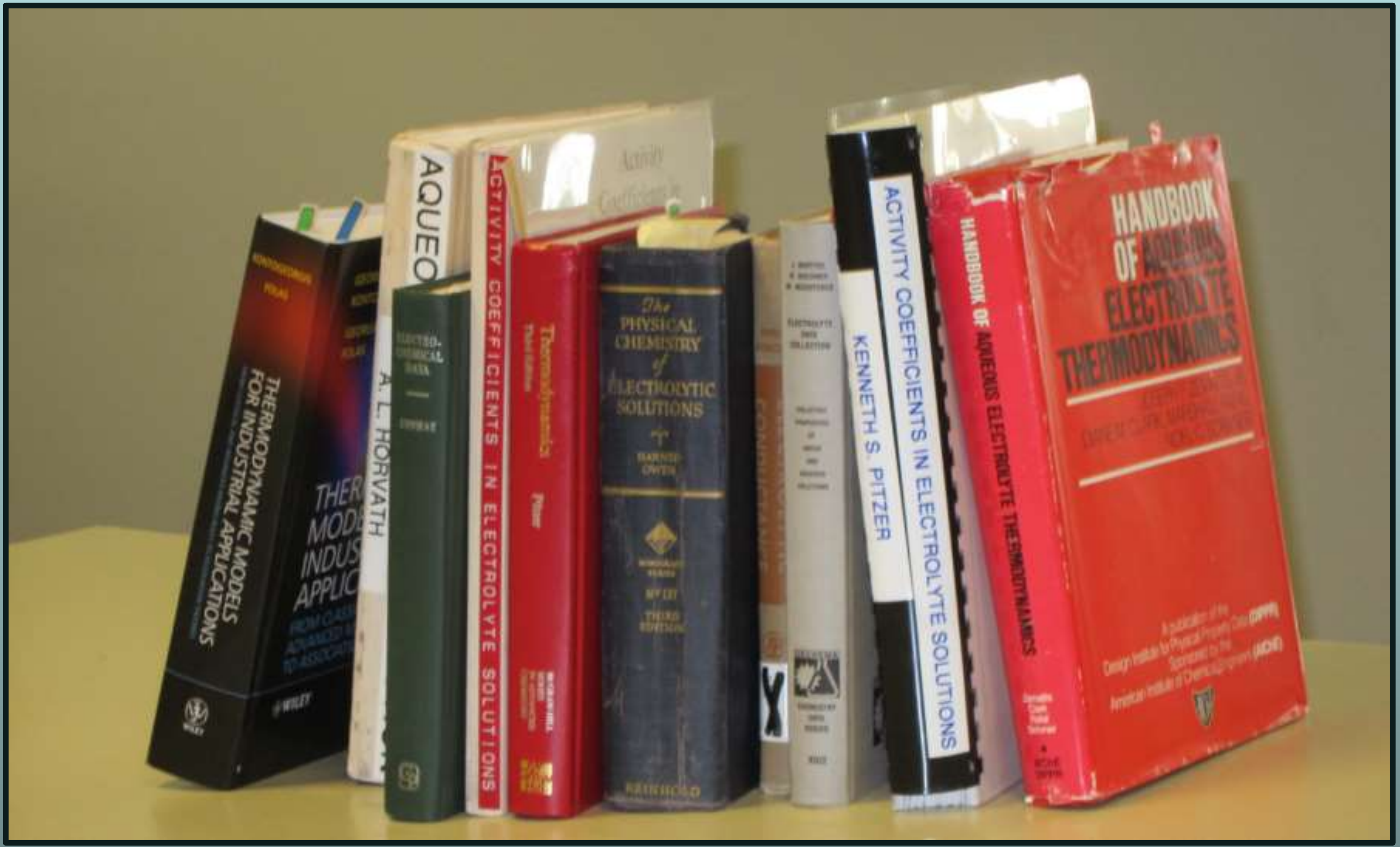
beyond a concentration of 0.1M or so."

The classical text of Robinson and Stokes
(not otherwise noted for its emotional content)
gives a glimpse of these feelings when it says

“In regard to concentrated solutions, many workers adopt a counsel of despair, confining their interest to concentrations below about 0.02 M, ... ”

p. 302 *Electrolyte Solutions* (1959) Butterworths , also Dover (2002)

Good Data


THERMODYNAMIC MODELS FOR INDUSTRIAL APPLICATIONS
AQUEO
A. L. HORVATH
ACTIVITY COEFFICIENTS IN ELECTROLYTE SOLUTIONS
The PHYSICAL CHEMISTRY of ELECTROLYTIC SOLUTIONS
REINHOLD
KENNETH S. PITZER
ACTIVITY COEFFICIENTS IN ELECTROLYTE SOLUTIONS
HANDBOOK OF AQUEOUS ELECTROLYTE THERMODYNAMICS
HANDBOOK OF AQUEOUS ELECTROLYTE THERMODYNAMICS

It is difficult to even define

in a unique way

Properties of One Ion

when

Everything

Interacts

with

Everything

Tremendous Opportunity for Applied Mathematics

Electrolytes are Complex Fluids

Hünenberger & Reif (2011)
"**Single-Ion Solvation**
… Approaches to **Elusive*** Thermodynamic Quantities"

After 690 pages and 2604 references, properties of

SINGLE Ions
are
Elusive*

because

Every Ion
Interacts
with
Everything

*'elusive' is in the authors' choice in the title but **emphasis** is added

Ions in Water are the Liquid of Life

They are not ideal solutions

Everything
Interacts
with
Everything

For Modelers and Mathematicians
Tremendous Opportunity for Applied Mathematics
because
'law' of mass action assumes nothing interacts
Chun Liu's Energetic Variational Principle
EnVarA

Good Data

Compilations of Specific Ion Effect

1. >139,175 Data Points [Sept 2011] *on-line*
IVC-SEP Tech Univ of Denmark
http://www.cere.dtu.dk/Expertise/Data_Bank.aspx

2. Kontogeorgis, G. and G. Folas, *2009:*
Models for Electrolyte Systems. Thermodynamic
John Wiley & Sons, Ltd. 461-523.

3. Zemaitis, J.F., Jr., D.M. Clark, M. Rafal, and N.C. Scrivner, *1986,*
Handbook of Aqueous Electrolyte Thermodynamics.
American Institute of Chemical Engineers

4. Pytkowicz, R.M., *1979,*
Activity Coefficients in Electrolyte Solutions. Vol. 1.
Boca Raton FL USA: CRC. 288.

Mathematics of Chemistry

must deal

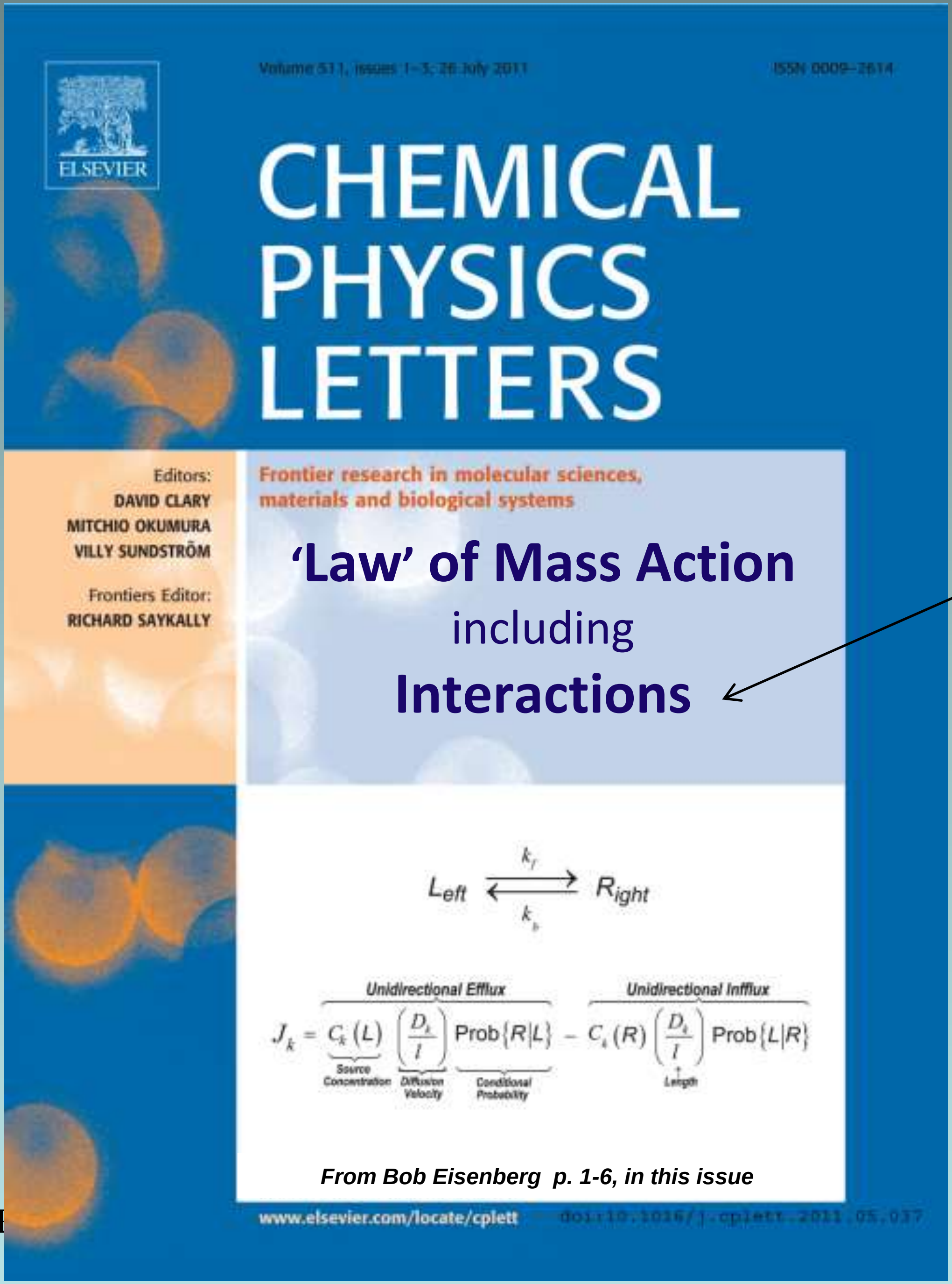
Naturally

with

Interactions

'Law of Mass Action' assumes nothing interacts

So this is a great opportunity for new mathematics and applications!



Mathematics
of
Interactions
in
Complex Fluids

Variational Approach
EnVarA

$$\overbrace{\frac{\delta \vec{E}}{\delta \vec{x}}}^{\textit{Conservative}} - \overbrace{\frac{1}{2}\frac{\delta \Delta}{\delta \vec{u}}}^{\textit{Dissipative}} = 0$$

Shielding
is a defining property of
Complex Fluids

It is VERY hard to Simulate at Equilibrium
and (in my opinion)
IMPOSSIBLE to Simulate in nonequilibrium
Like Batteries or Nerve Fibers
because flows involve
Far Field (macroscopic) boundaries

Main Qualitative Result

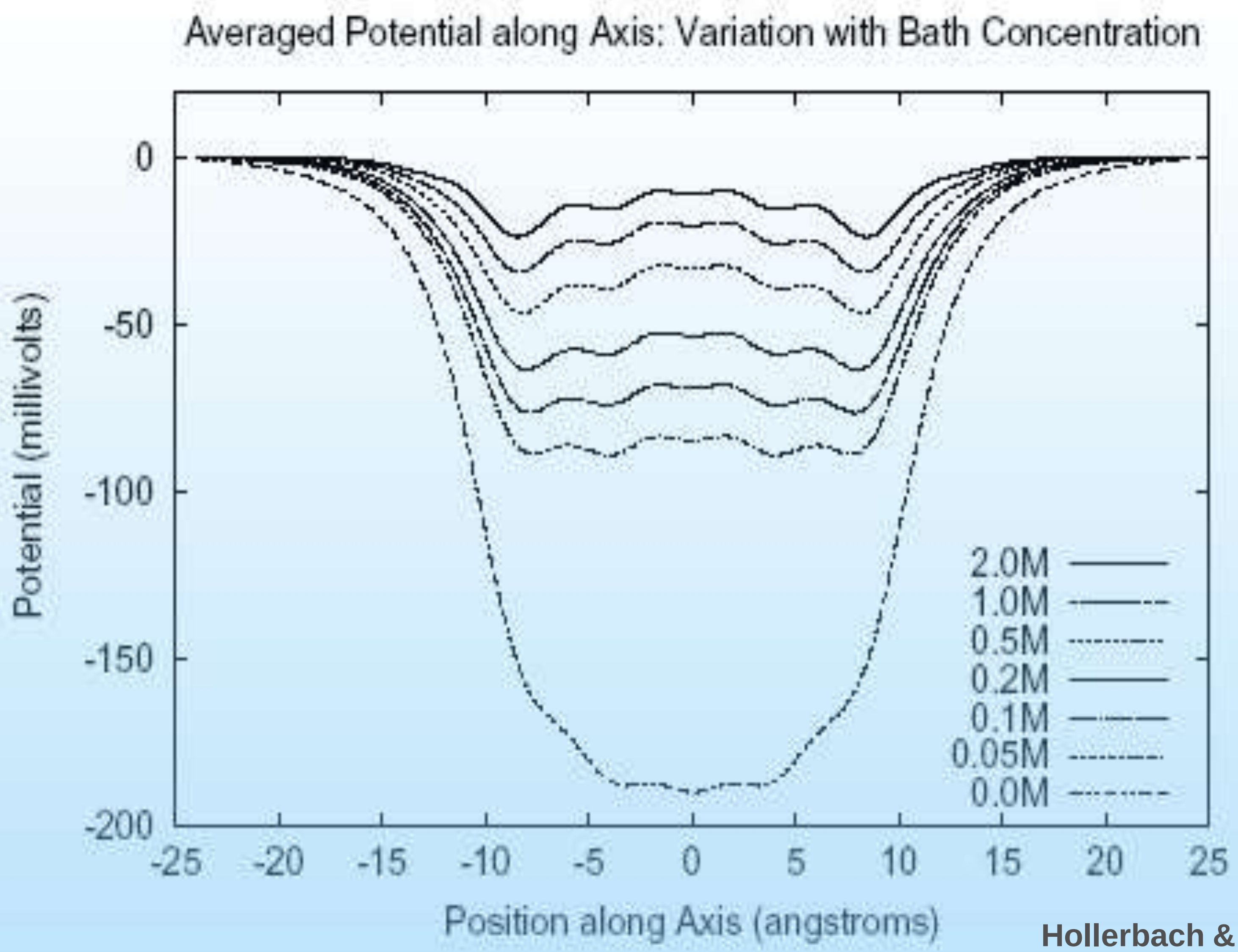
Shielding Dominates
Electric Properties of Channels, Proteins, as it does Ionic Solutions

Shielding is ignored in traditional treatments

of Ion Channels and of Active Sites of proteins

Rate Constants Depend on Shielding
and so
Rate Constants Depend on Concentration and Charge

Main Qualitative Result
Shielding in Gramicidin



Hollerbach & Eisenberg

Reconciling

Mass Action

and

Maxwell/Kirchoff

will no doubt be a

Long Journey

“ … incomplete truths
learned on the way
may become ingrained

and taken as the whole truth…….

what is true
and what is only sometimes true
will become confused.”

Richard Feynman
from p.15-61 “The Feynman: Lectures on Physics, Mainly Electromagnetism and Matter. Vol. 2” 1963, New York: Addison-Wesley Publishing Co., also at available on line

“Sometimes it is necessary to put a veil on the past, For the Sake of the Future”

Henry Clay, the Essential American
p. 375 D.S. & J.T. Heidler

“Journey

of a thousand miles

starts

with a single step”

in the right direction,

I beg to add to this Chinese saying

As a Chicago Surgeon put it

You better head in the right direction,

if you want to get anywhere

That direction needs to include the

Electric Field

calculated and calibrated,
global and local,

if the journey is ever to end,
in my view.

Replacement of
“Law of Mass Action”
is
Feasible for
<u>Ionic Solutions</u>

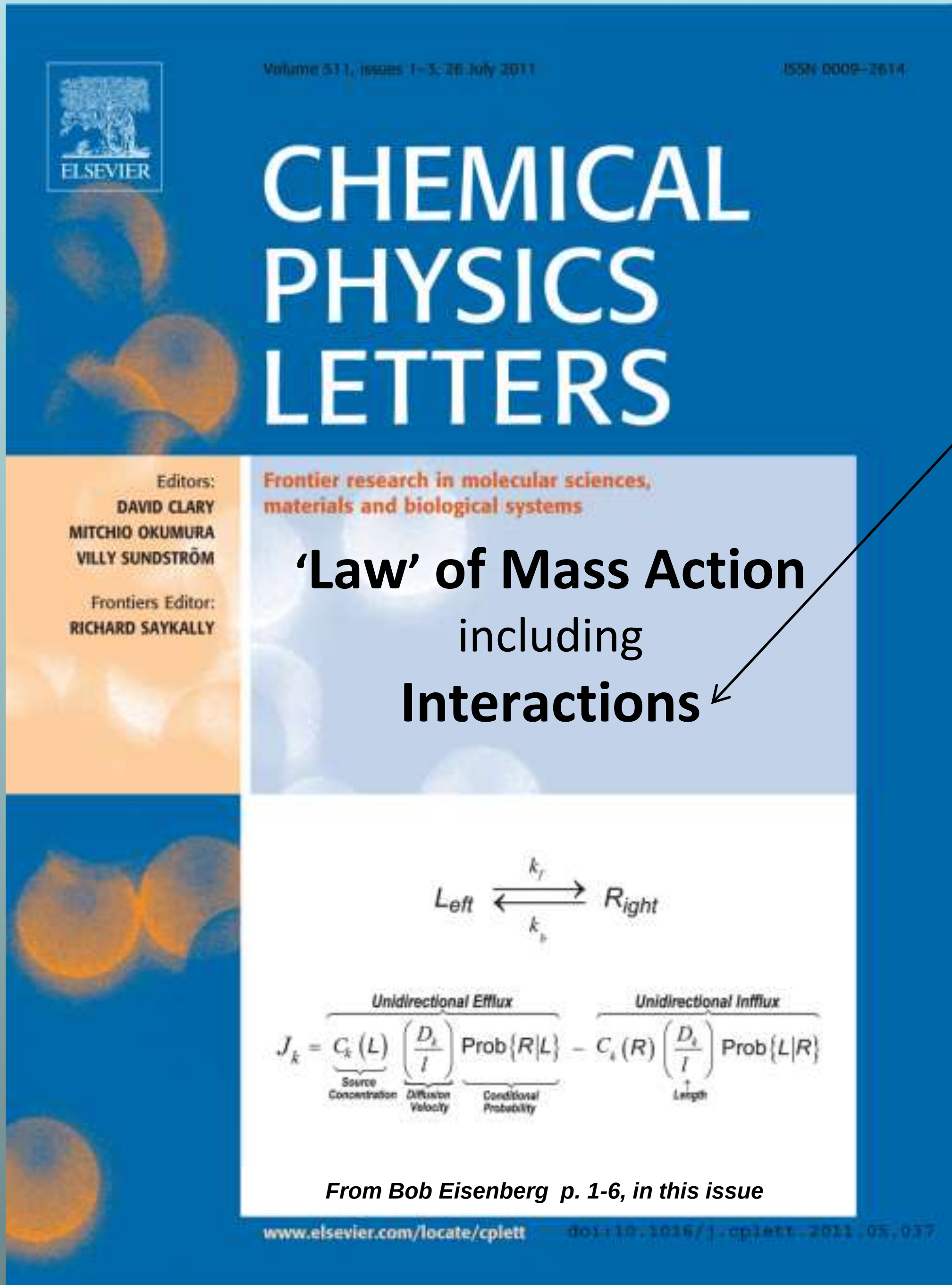
using the

<u>All Spheres</u>

(primitive = implicit solvent model of ionic solutions)

and

<u>Theory of Complex Fluids</u>



Variational Approach
EnVarA

Conservative ***Dissipative***

$$\overbrace{\frac{\delta E}{\delta \vec{\boldsymbol{x}}}} - \overbrace{\frac{1}{2}\frac{\delta \Delta}{\delta \vec{\boldsymbol{u}}}} = 0$$

Energetic Variational Approach allows

accurate computation of

Flow and Interactions

in Complex Fluids like Liquid Crystals

Classical theories and Molecular Dynamics have difficulties with flow, interactions, and complex fluids

Engineering needs Calibrated Theories and Simulations

Engineering Devices almost always use flow

Energetic Variational Approach

EnVarA

Chun Liu, Rolf Ryham, and Yunkyong Hyon

Mathematicians and Modelers: two different 'partial' variations written in one framework, using a 'pullback' of the action integral

Conservative 'Force' — Dissipative 'Force'

Shorthand for Euler Lagrange process with respect to $\vec{x}$

Shorthand for Euler Lagrange process with respect to $\vec{u}$

$$\frac{\delta E}{\delta \vec{\mathbf{x}}} - \frac{1}{2}\frac{\delta \Delta}{\delta \vec{\mathbf{u}}} = 0$$

Action Integral, *after pullback*

Rayleigh Dissipation Function

Composite

Variational Principle

⇕

Euler Lagrange Equations

Field Theory of Ionic Solutions: Liu, Ryham, Hyon, Eisenberg

Allows boundary conditions and flow

Deals Consistently with Interactions of Components

Dissipation Principle

Conservative Energy dissipates into Friction

Conservative

$$\frac{d}{dt}\int\left\{k_BT\sum_{i=n,p}c_i\log c_i+\frac{1}{2}\left(\rho_0+\sum_{i=n,p}z_iec_i\right)\phi+\sum_{i,j=n,p}\frac{c_i}{2}\int\tilde{\Psi}_{i,j}\;c_j\,d\vec{y}\right\}d\vec{x}$$

time; Thermal Energy; Number Density; Permanent Charge of protein; Hard Sphere Terms

$$=\;-\int\left\{\sum_{i=n,p}\frac{D_ic_i}{k_BT}\left|k_BT\frac{\nabla c_i}{c_i}+z_ie\nabla\phi-\sum_{j=n,p}\nabla\int\tilde{\Psi}_{i,j}\;c_j\,d\vec{y}\right|^2\right\}d\vec{x}$$

valence; proton charge; Hard Sphere Terms

Dissipative

c_i number density; k_BT thermal energy; D_i diffusion coefficient; n negative; p positive; z_i valence; ε dielectric constant

Note that $\varepsilon\frac{|\nabla\phi|^2}{2}=\frac{1}{2}\left(\rho_0+\sum_{i=n,p}z_iec_i\right)\phi$ **with suitable boundary conditions**

Energetic Variational Approach

EnVarA

$$\underbrace{\frac{\delta E}{\delta \vec{\mathbf{x}}}}_{\text{Conservative 'Force'}} - \underbrace{\frac{1}{2}\frac{\delta \Delta}{\delta \vec{\mathbf{u}}}}_{\text{Dissipative 'Force'}} = 0$$

is defined by the Euler Lagrange Process,

as I understand the pure math from Craig Evans

which gives

Equations like PNP

BUT

I leave it to you (all)

to argue/discuss with Craig

about the purity of the process

when two variations are involved

PNP (Poisson Nernst Planck) for Spheres

Non-equilibrium variational field theory *EnVarA*

Nernst Planck Diffusion Equation

*for **number density c_n** of negative n ions; positive ions are analogous*

$$\frac{\partial c_n}{\partial t} = \nabla \cdot \left[D_n \left\{ \nabla c_n + \frac{c_n}{k_B T} \left(z_n e \nabla \phi - \int \frac{12\varepsilon_{n,n}(a_n + a_n)^{12}(\vec{x} - \vec{y})}{|\vec{x} - \vec{y}|^{14}} c_n(\vec{y}) d\vec{y} - \int \frac{6\varepsilon_{n,p}(a_n + a_p)^{12}(\vec{x} - \vec{y})}{|\vec{x} - \vec{y}|^{14}} c_p(\vec{y}) d\vec{y} \right) \right\} \right],$$

Diffusion Coefficient

Thermal Energy

Coupling Parameters

Ion Radii

Number Densities

Poisson Equation

$$\nabla \cdot (\varepsilon \nabla \phi) = -\left(\rho_0 + \sum_{i=1}^{N} z_i e c_i \right) \qquad i = n \text{ or } p$$

Dielectric Coefficient

valence
proton charge

Permanent Charge of Protein

Eisenberg, Hyon, and Liu

Semiconductor *PNP* Equations

For Point Charges

Poisson's Equation

Dielectric Coefficient

Permanent Charge of Protein

$$-\frac{\varepsilon_0}{A(x)}\frac{d}{dx}\left(\varepsilon(x)A(x)\frac{d\phi}{dx}\right)=e\mathrm{P}(x)+e\sum_i z_i\rho_i(x)$$

Cross sectional Area

Valence
Proton charge

Drift-diffusion & Continuity Equation

Number Densities

$$\frac{dJ_i}{dx}=0 \qquad -J_i=D_i(x)A(x)\rho_i(x)\frac{d\mu_i}{dx}$$

Flux

Diffusion Coefficient

Chemical Potential $\mu_i(x)$

$$\mu_i(\mathrm{x})=z_i e\phi(\mathrm{x})+kT\ln\left(\frac{\rho_i(\mathrm{x})}{\rho^*}\right)+\underbrace{\mu_i^{\mathrm{ex}}(\mathrm{x})}_{\text{Finite Size, Special Chemistry}}$$

Not in Semiconductor

Finite Size
Special Chemistry

valence
proton charge

Thermal Energy

All we have to do is

Solve them!

with Boundary Conditions

defining

Charge Carriers

ions, holes, quasi-electrons

Geometry

Solution* of PNP Equation

$$J_k = \overbrace{\underbrace{C_k(L)}_{\text{Source Concentration}}\underbrace{\underbrace{\left(\frac{D_k}{\lambda}\right)}_{\text{Diffusion Velocity}}\underbrace{\mathrm{Prob}\{R|L\}}_{\text{Conditional Probability}}}_{\text{Rate Constant}}}^{\text{Unidirectional Efflux}} - \overbrace{C_k(R)\left(\frac{D_k}{\lambda}\right)\mathrm{Prob}\{L|R\}}^{\text{Unidirectional Infflux}}$$

↑ Channel Length (λ)

***MATHEMATICS**

This solution was **actually DERIVED** by computing many conditional probability measures explicitly by repeated **analytical** integrations

Eisenberg, Klosek, & Schuss (1995) *J. Chem. Phys.* 102, 1767-1780

Eisenberg, B. (2000) in Biophysics Textbook On Line "Channels, Receptors, and Transporters"

Eisenberg, B. (2011). Chemical Physics Letters 511: 1-6

Please do not be deceived
by the eventual simplicity of Results.
This took >2 years!

Solution

was actually

DERIVED

with explicit formulae

for probability measures

from a

Doubly Conditioned Stochastic Process

involving

Analytical Evaluation

of

Multidimensional Convolution Integrals

Eisenberg, Klosek, & Schuss (1995) *J. Chem. Phys.* 102, 1767-1780
Eisenberg, B. (2000) in Biophysics Textbook On Line "Channels, Receptors, Transporters"
Eisenberg, B. (2011). Chemical Physics Letters 511: 1-6

All we have to do is
Solve them!

Don't Despair

Semiconductor Technology has Already Done That!

Semiconductor Devices

PNP equations describe many robust input output relations

Amplifier
Limiter
Switch
Multiplier
Logarithmic convertor
Exponential convertor

These are SOLUTIONS of PNP for different boundary conditions with ONE SET of CONSTITUTIVE PARAMETERS

PNP of POINTS is TRANSFERRABLE

Analytical should be attempted using techniques of

Weishi Liu University of Kansas

Tai-Chia Lin National Taiwan University & **Chun Liu** PSU

The End

Any Questions?